

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2003-267719

(43)Date of publication of application : 25.09.2003

(51)Int.Cl.

C01B 33/12
B01D 39/16
B01D 39/20
B01D 69/10
B01D 71/02
B01D 71/70
B01J 20/10
B01J 20/28
B01J 39/08
B01J 47/12
C01B 33/16

(21)Application number : 2002-072355 (71)Applicant : NIPPON STEEL CORP

(22)Date of filing : 15.03.2002 (72)Inventor : YAMADA NORIKO
KATAYAMA SHINGO(54) POROUS BODY, BASE BODY HAVING POROUS BODY FILM, AND THEIR
MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a porous body which can be simply dried under a normal pressure without requiring a supercritical drying and made porous at a low temperature, and whose surface can be made active.

SOLUTION: A solution is prepared by dissolving one or more kinds selected from a metallic or metalloid alkoxide expressed by the general formula: $M(OR_1)_n$, an organoalkoxysilane expressed by the general formula: $Si(R_2)_m(OR_3)_{4-m}$, and a polyorganosiloxane expressed by the general formula: $HO-[Si(R_4)_2O]_l-H$, and $H_xSi(R_5)_y(OR_6)_{4-x-y}$ in an organic solvent. In a manufacturing method for the porous body, the prepared solution is hydrolyzed or partially hydrolyzed, gelated, and dried to become the porous body. The content of the $H_xSi(R_5)_y(OR_6)_{4-x-y}$ based on the total mole number of the metals or metalloids in the solution is, in terms of Si, ≥ 10 mol% and ≤ 90 mol%. The porous body thus obtained is provided.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of
rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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JAPANESE

[JP,2003-267719,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1] General formula $M(OR_1)_n$ (M is the element of a metal or semimetal and R_1 is a with a carbon numbers of one or more organic radical) The alkoxide of the metal by which n is expressed with the valence of a metal or semimetal, or semimetal, General formula $Si(R_2)_m(OR_3)_{4-m}$ (R_2 and R_3 are with a carbon numbers of one or more organic radicals) m is organoalkoxysilane and general formula $HO-[Si(R_4)_2O]_l-H$ (R_4 is a with a carbon numbers of one or more organic radical) expressed with the integer of 1-3. One sort or two sorts or more which are chosen from the polyorganosiloxane to which l is expressed with the integer of 2-500, $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) They are hydrolysis or a method of carrying out partial hydrolysis, gelling and drying and manufacturing a porous body about the solution which dissolved $x+y \leq 4$ in the organic solvent. The content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ by Si conversion The manufacture approach of the porous body characterized by being less than [more than 10 mol % 90 mol %] to the total number of mols of the metal in said solution, or semimetal.

[Claim 2] The manufacture approach of a porous body according to claim 1 of performing said gelation and desiccation in a -50 degrees C - 150 degrees C temperature requirement, respectively.

[Claim 3] It is $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) to a silicate water solution. The manufacture approach of the porous body characterized by being the approach of gelling the solution which added $x+y \leq 4$, drying and manufacturing a porous body, and the content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ being below 80 mass % more than 5 mass % to the total mass of said solution in Si conversion.

[Claim 4] It is $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) to the colloid water solution of an oxide particle. The manufacture approach of the porous body characterized by being the approach of gelling the solution which added $x+y \leq 4$, drying and manufacturing a porous body, and the content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ being below 80 mass % more than 5 mass % in Si conversion to the total mass of said solution.

[Claim 5] The manufacture approach of the porous body according to claim 3 or 4 which dries in a room temperature -150 degree C temperature requirement by performing said gelation in a -50 degrees C - 50 degrees C temperature requirement.

[Claim 6] The porous body characterized by being the porous body obtained by the approach according to claim 1 to 5, and for the porosity of this porous body being 40 - 99.9%, and specific surface area being more than 50m²/g.

[Claim 7] The porous body according to claim 6 whose average pore diameter the pore of said porous body is 5nm - 5mm including the micropore of 5-100nm of apertures, and the pore of 100 micrometers - 5mm of apertures.

[Claim 8] General formula $M(OR_1)_n$ (M is the element of a metal or semimetal and R_1 is a with a carbon numbers of one or more organic radical) The alkoxide of the metal by which n is expressed with the valence of a metal or semimetal, or semimetal, General formula $Si(R_2)_m(OR_3)_{4-m}$ (R_2 and R_3 are with a carbon numbers of one or more organic radicals) m is organoalkoxysilane and general formula $HO-[Si(R_4)_2O]_l-H$ (R_4 is a with a carbon numbers of one or more organic radical)

expressed with the integer of 1-3. One sort or two sorts or more which are chosen from the polyorganosiloxane to which 1 is expressed with the integer of 2-500, $\text{H}_x\text{Si}(\text{R}_5)_y(\text{OR}_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) This solution is applied to a base after hydrolyzing the solution which dissolved $x+y \leq 4$ in the organic solvent. Are the approach of manufacturing the base which gels, dries and has the porous body film, and the content of said $\text{H}_x\text{Si}(\text{R}_5)_y(\text{OR}_6)_{4-x-y}$ receives the total number of mols of the metal in said solution, or semimetal. The manufacture approach of a base of having the porous body film characterized by being less than [more than 10 mol % 90 mol %] by Si conversion.

[Claim 9] The manufacture approach of a base of having the porous body film according to claim 8 which performs said gelation and desiccation in a -50 degrees C - 150 degrees C temperature requirement, respectively.

[Claim 10] The base which has the porous body film characterized by being the base which has the porous body film obtained by the approach according to claim 8 or 9, and for the porosity of said porous body film being 40 - 99.9%, and specific surface area being more than 50m²/g.

[Claim 11] The base with which the pore of said porous body film has the porous body film according to claim 10 whose average pore diameter is 5nm - 5mm including the micropore of 5-100nm of apertures, and the pore of 100 micrometers - 5mm of apertures.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a porous body ingredient applicable to a filter, a demarcation membrane, a sensor, an adsorbent, a catalyst and catalyst support, immobilized enzyme support, an ion exchanger, a heat insulator, an insulator, etc., and its manufacture approach about the porous body of the glass obtained by the sol-gel method, or the ceramics, the bases which have the porous body film, and these manufacture approaches.

[0002]

[Description of the Prior Art] Porous bodies, such as a metal, glass, ceramics, and an organic polymer, are used for a filter, a demarcation membrane, a sensor, an adsorbent, a catalyst and catalyst support, immobilized enzyme support, the ion exchanger, the heat insulator, the insulator, the separation column, etc. by choosing the quality of the material, hole size, hole surface qualification, etc.

[0003] There are the aerogel produced with a sol-gel method by using an alkoxide as a raw material, xerogel, phase separation gel, an organic functional-group template porous body, a micell porous body, etc. as porous body of glass or the ceramics.

[0004] Aerogel is a porous body which hydrolyzes alkoxides, such as silicon, is dried using the supercritical fluid of after gelation, alcohol, or carbon dioxide gas, and is obtained.

[0005] Xerogel hydrolyzes alkoxides, such as silicon, since it is easy to generate a crack with the surface tension of the solvent within pore after gelation in case gel is seasoned naturally although it is the porous body seasoned naturally and obtained, adds a desiccation control agent (it is written as DCCA Drying Control Chemical Additive and the following), and is made to gel them in many cases.

[0006] Phase separation gel is a porous body made gel the sol containing organic macromolecules, such as polyethylene oxide (PEO), calcinated and obtained, and an organic macromolecule and inorganic gel are the porous bodies in which pore is formed by pyrolyzing an organic part by the lifting and baking in phase separation in a gelation process.

[0007] An organic functional-group template porous body is a porous body calcinated [hydrolyzes the alkoxide containing organoalkoxysilane, gels and] and obtained, and is a porous body in which pore is formed by using the organic functional group coupled directly with silicon as a template for forming pore, and pyrolyzing an organic functional group.

[0008] After a micell porous body's including a surfactant in the sol which hydrolyzed the alkoxide and making it gel, it is a porous body calcinated and obtained and is a porous body in which a surfactant forms micellar structure in in self-organization, and pore is formed by pyrolyzing a surfactant.

[0009]

[Problem(s) to be Solved by the Invention] Since it is producible at low temperature, although an activity front face is obtained, since a supercritical drying process is needed, aerogel needs high pressure installation. On the other hand, although phase separation gel, an organic functional-group template porous body, and a micell porous body do not need special equipment in a desiccation process, since they need the baking process by the elevated temperature for pyrolyzing the organic substance, an activity front face is hard to be obtained and a part for organic and carbon tend to

remain.

[0010] Since it is producible by drying the gel obtained by mainly carrying out the hydrolysis and the polycondensation of the tetra-ethoxy silane by the acid or the base catalyst near ordinary temperature, although an activity front face is easy to be obtained, in order to be easy to generate a crack especially with the internal stress at the time of desiccation and to prevent crack initiation from the reinforcement of the silica frame of gel being low lacking in flexibility, xerogel must add DCCA and must control desiccation conditions with high precision. In the xerogel which adds organoalkoxysilane to a tetra-ethoxy silane and is obtained in order to ease the internal stress which gives flexibility to a silica frame and is generated, since it has flexibility by the organic radical combined with a silica frame, although it is hard coming to generate a crack at the time of desiccation, since the reinforcement of gel is not enough, careful desiccation may have to be performed and the yield may worsen.

[0011] This invention improves the trouble in the porous body and its manufacture approach of the glass produced by the above-mentioned sol-gel method, or the ceramics, does not need a supercritical drying process in the production process, but since it can carry out [porosity]-izing at low temperature, it aims at offering the porous body which has an activity front face, while offering the manufacture approach which can be dried simple by low-temperature ordinary pressure.

[0012]

[Means for Solving the Problem]

In order to attain said purpose, the invention in this application makes the following modes a summary. (1) General formula $M(OR_1)_n$ (M is the element of a metal or semimetal and R_1 is a with a carbon numbers of one or more organic radical) The alkoxide of the metal by which n is expressed with the valence of a metal or semimetal, or semimetal, General formula $Si(R_2)_m(OR_3)_{4-m}$ (R_2 and R_3 are with a carbon numbers of one or more organic radicals) m is organoalkoxysilane and general formula $HO-[Si(R_4)_2O]_l-H$ (R_4 is a with a carbon numbers of one or more organic radical) expressed with the integer of 1-3. One sort or two sorts or more which are chosen from the polyorganosiloxane to which l is expressed with the integer of 2-500, $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) They are hydrolysis or a method of carrying out partial hydrolysis, gelling and drying and manufacturing a porous body about the solution which dissolved $x+y \leq 4$ in the organic solvent. The content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ by Si conversion The manufacture approach of the porous body characterized by being less than [more than 10 mol % 90 mol %] to the total number of mols of the metal in said solution, or semimetal.

(2) The manufacture approach of a porous body given in (1) of performing said gelation and desiccation in a -50 degrees C - 150 degrees C temperature requirement, respectively.

(3) It is $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) to a silicate water solution. The manufacture approach of the porous body characterized by being the approach of gelling the solution which added $x+y \leq 4$, drying and manufacturing a porous body, and the content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ being below 80 mass % more than 5 mass % to the total mass of said solution in Si conversion.

(4) It is $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) to the colloid water solution of an oxide particle. The manufacture approach of the porous body characterized by being the approach of gelling the solution which added $x+y \leq 4$, drying and manufacturing a porous body, and the content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ being below 80 mass % more than 5 mass % to the total mass of said solution in Si conversion.

(5) (3) which dries in a room temperature -150 degree C temperature requirement by performing said gelation in a -50-50-degree C temperature requirement, or the manufacture approach of a porous body given in (4).

(6) (1) Porous body characterized by being the porous body obtained by the approach of a publication by either of - (5), and for the porosity of this porous body being 40 - 99.9%, and specific surface area being more than 50m²/g.

(7) said -- a porous body -- pore -- an aperture -- five - 100 -- nm -- micropore -- and -- an aperture --

100 -- micrometer - five -- mm -- pore -- containing -- an average -- a pore diameter -- five -- nm - five -- mm -- it is -- (-- six --) -- a publication -- a porous body .

(8) General formula $M(OR_1)_n$ (M is the element of a metal or semimetal and R_1 is a with a carbon numbers of one or more organic radical) The alkoxide of the metal by which n is expressed with the valence of a metal or semimetal, or semimetal, General formula $Si(R_2)_m(OR_3)_{4-m}$ (R_2 and R_3 are with a carbon numbers of one or more organic radicals) m is organoalkoxysilane and general formula $HO-[Si(R_4)_2O]_l-H$ (R_4 is a with a carbon numbers of one or more organic radical) expressed with the integer of 1-3. One sort or two sorts or more which are chosen from the polyorganosiloxane to which l is expressed with the integer of 2-500, $H_xSi(R_5)_y(OR_6)_{4-x-y}$ (R_5 and R_6 are with a carbon numbers of one or more organic radicals, x is the integer of 1-3 and y is the integer of 0-3) This solution is applied to a base after hydrolyzing the solution which dissolved $x+y \leq 4$ in the organic solvent. Are the approach of manufacturing the base which gels, dries and has the porous body film, and the content of said $H_xSi(R_5)_y(OR_6)_{4-x-y}$ receives the total number of mols of the metal in said solution, or semimetal. The manufacture approach of a base of having the porous body film characterized by being less than [more than 10 mol % 90 mol %] by Si conversion.

(9) The manufacture approach of a base of having the porous body film given in (8) which performs said gelation and desiccation in a -50 degrees C - 150 degrees C temperature requirement, respectively.

(10) The base which has the porous body film characterized by being the base which has the porous body film obtained by (8) or (9) by the approach of a publication, and for the porosity of said porous body film being 40 - 99.9%, and specific surface area being more than 50m²/g.

(11) said -- a porous body -- the film -- pore -- an aperture -- five - 100 -- nm -- micropore -- and -- an aperture -- 100 -- micrometer - five -- mm -- pore -- containing -- an average -- a pore diameter -- five -- nm - five -- mm -- it is -- (-- ten --) -- a publication -- a porous body -- the film -- having -- a base .

[0013]

[Embodiment of the Invention] The alkoxide of the metal used for this invention or semimetal is expressed with chemical formula $M(OR_1)_n$. M is the element of a metal or semimetal, for example, it is B, Si, aluminum, Ti, Zr, Ta, Nb, Y, Co, Fe, W, Mo, Cr, Mn, Re, Mg, Sr, Ba, calcium, K, Na, La, Ce, etc. here, and n is the valence of the element M of a metal or semimetal. Although R_1 is a with a carbon numbers of one or more organic radical, and it is the organic radical of carbon numbers 1-8 preferably and not being limited especially as an alkoxy group (-OR₁), a methoxide, ethoxide, propoxide, butoxide, etc. are mentioned, for example. All the alkoxy groups in the alkoxide ($M(OR_1)_n$) 1 molecule of a metal or semimetal may be the same, or may differ. the alkoxide of said metal or semimetal -- one sort -- or two or more sorts can be used, and a part of alkoxy group may be permuted and used by beta-diketone, beta-keto ester, alkanolamine, alkyl alkanolamine, an organic acid, etc.

[0014] Although the organoalkoxysilane used for this invention is expressed with chemical formula $Si(R_2)_m(OR_3)_{4-m}$, m is the integer of 1-3 and R_2 and R_3 are with a carbon numbers of one or more organic radicals, as for R_2 , it is desirable that it is carbon numbers 1-8, and is the organic radical which may also contain different elements, such as N, O, and S, and, as for R_3 , it is desirable that it is the organic radical of carbon numbers 1-8. An organic radical (-R₂) - CH₃, -C₂H₅, -C₃H₇, -C₄H₉, -CH=CH₂, -C₆H₅, -CF₃, -C₂F₅, -C₃F₇, -C₄F₉, -CH₂CH₂CF₃, -CH₂CH₂C₆F₁₃, -CH₂CH₂C₈F₁₇, -C₃H₆NH₂ It is -C₃H₆NHC₂H₄NH₂, -C₃H₆OCH₂CHOCH₂, and -C₃H₆OCOC(CH₃)=CH₂ grade, and an alkoxy group (-OR₃) consists of a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. Two or more organic radicals and alkoxy groups may be different radicals when it exists by the same intramolecular, respectively.

[0015] It may be beforehand used with the water below equimolar to the total number of mols of the alkoxy group in this organoalkoxysilane, hydrolyzing or carrying out partial hydrolysis of the organoalkoxysilane.

[0016] With the polyorganosiloxane used for this invention It is the polymer expressed with chemical formula $HO-[Si(R_4)_2O]_l-H$. R_4 is a with a carbon numbers of one or more organic radical. Preferably Carbon numbers 1-8N, It may be the organic radical which may also contain

different elements, such as O and S, and it may consist of -CH₃, -C₂H₅, -C₃H₇, -C₄H₉, -CH=CH₂, and -C₆H₅ grade, and an organic radical (-R₄) may be a different organic radical. As an example of this polyorganosiloxane, poly dimethylsiloxane, the poly diethyl siloxane, the poly dipropyl siloxane, a poly diphenyl siloxane, a poly methylphenyl siloxane, etc. are mentioned. As for l of said chemical formula, 500 or less [2 or more] are desirable. Less than two, l is the same as the hydrolysis condition of organoalkoxysilane, and means organoalkoxysilane. On the other hand, if l exceeds 500, the rate of stopping being able to dissolve in a solvent easily and occupying in the polymer of the hydroxyl group which is a reacting point will decrease, and it will be hard coming to compound the gel of inorganic and an organic hybrid.

[0017] As for HxSi(R₅) y(OR₆)_{4-x-y} used for this invention, R₅ and R₆ are with a carbon numbers of one or more organic radicals, and x is the integer of 1-3, y is the integer of 0-3, and it is x+y≤4. R₅ is the organic radical which may also contain different elements, such as N, O, and S, with carbon numbers 1-8, and, as for R₆, it is preferably desirable that it is the organic radical of carbon numbers 1-8. Alkoxy groups (-OR₆) are a methoxy group, an ethoxy radical, a propoxy group, a butoxy radical, etc. an organic radical (-R₅) - CH₃, -C₂H₅, -C₃H₇, -C₄H₉, -CH=CH₂, -C₆H₅, -CF₃, -C₂F₅, -C₃F₇, -C₄F₉, -CH₂CH₂CF₃, -CH₂CH₂C₆F₁₃, -CH₂CH₂C₈F₁₇, -C₃H₆NH₂, -C₃H₆NHC₂H₄NH₂, -C₃H₆OCH₂CHOCH₂, and -C₃H₆OCOC(CH₃)=CH₂ grade are mentioned. As for x of said chemical formula, 1-3 are desirable, and less than by one, 0 [i.e.,], since Si-H is lost, reactivity worsens. On the other hand, by ***** 4 which x exceeds three, reactivity is too high and it is hard to treat. y of said chemical formula is 0-3, and especially 0-2 are desirable. In ***** 4 which y exceeds three, since reactant Si-H and reactant Si-OR are lost, a reaction will not advance. By the electronic suction nature of H, since the hydrolysis reactivity of an alkoxy group is high, if HxSi(R₅) y(OR₆)_{4-x-y} exists, it will gel easily, and the gel of high intensity is formed, and a crack stops easily being able to produce HxSi(R₅) y(OR₆)_{4-x-y} which has H-Si at the time of desiccation. Moreover, if it reacts under basicity, it will gel by the rapid reaction accompanied by generating of H₂ gas of H-Si, also forming macropore, and the so-called foam will be formed.

[0018] The alkoxide of the metal expressed with said general formula M(OR₁)_n, or semimetal, The organoalkoxysilane expressed with said general formula Si(R₂) m(OR₃)_{4-m}, One sort chosen from the polyorganosiloxane expressed with said general formula HO-[Si(R₄)₂O]_l-H or two sorts or more, and said HxSi(R₅) y(OR₆)_{4-x-y} can be set in the solution which dissolved in the organic solvent. As for the content of said HxSi(R₅) y(OR₆)_{4-x-y}, less than [more than 10 mol %90 mol %] is desirable at Si conversion to the total number of mols of the metal in said solution, or semimetal. Less than [10 mol %], it is easy to generate a crack at the time of desiccation, and a porous body with a high specific surface area is not obtained. On the other hand, if 90-mol % is exceeded, the reinforcement of gel will become weak and the independent gel without a crack will not be obtained.

[0019] Alkoxide M(OR₁)_n [which is used by this invention], organoalkoxysilane Si(R₂) m(OR₃)_{4-m}, and polyorganosiloxane HO-[Si(R₄)₂O]_l-H may be used independently, respectively, and may be mixed and used. the silicon especially combined with the organic radical (R₂, R₄) of organoalkoxysilane Si(R₂) m(OR₃)_{4-m} and the polyorganosiloxane HO-[Si(R₄)₂O]_l-H origin -- the whole quantity of said alkoxide, said organoalkoxysilane and one or more sorts of metallic elements of said polyorganosiloxane, or a semimetal element -- receiving -- more than 5 mol % -- it is easy to make the independent gel in which a crack does not have the way to include.

[0020] Hydrolysis or partial hydrolysis of alkoxide M(OR₁)_n [of the metal in this invention or semimetal], organoalkoxysilane Si(R₂) m(OR₃)_{4-m}, and polyorganosiloxane HO-[Si(R₄)₂O]_l-H and HxSi(R₅) y(OR₆)_{4-x-y} is performed by adding twice as many 1 - 100-mol water as this to the total number of mols of an alkoxy group. Water may be diluted with organic solvents, such as alcohol, and 500 or less times of a dilution ratio are desirable. If 500 times are exceeded, an addition total amount is too large, and the time amount added by dropping etc. is taken and it is not realistic.

[0021] In case water is added, an inorganic acid, organic acids, or those both are used as a catalyst. Although especially an inorganic acid is not limited, a hydrochloric acid, a sulfuric acid, a nitric acid, and a phosphoric acid are mentioned, for example. Although especially an organic acid is not limited, CH₃COOH, HCOOH, C₂H₅COOH, CF₃COOH, and CH₃SO₃H are mentioned, for example. These acid catalysts are 0.005-1 mol-double-added to the total number of mols of an

alkoxy group. In less than 0.005 mols, advance of a reaction is too slow and is not realistic. On the other hand, when one mol is exceeded, the amount of the acid which remains increases and the removal is needed.

[0022] In the partial hydrolysis of said raw material, or hydrolysis Alkoxide $M(OR)_n$ of a metal or semimetal, organoalkoxysilane $Si(R)_m(OR)_{4-m}$, Polyorganosiloxane $HO-[Si(R)_2O]_l-H$ and $H_xSi(R)_y(OR)_{4-x-y}$ are distributed to homogeneity. The organic solvent which can dissolve may be used, for example, it may be ketones, such as various alcohol, such as a methanol, ethanol, propanol, a butanol, methoxy ethanol, and ethoxy ethanol, and an acetone, toluene, a xylene, etc., and these mixed solvents are sufficient. Although especially the amount of the solvent which can be used is not limited, its 1000 or less times are desirable to the capacity of a raw material. If 1000 times are exceeded, even if it condenses in order not to gel if it remains as it is, but to make it gel, gelation will take time amount too much. Moreover, a solvent, the alcohol generated by hydrolysis may be distilled off and condensed under ordinary pressure or reduced pressure after hydrolysis.

[0023] Mixing, hydrolysis, or after carrying out partial hydrolysis, this solution is gelled and dried for said raw material at -50-150 degrees C. Since reactivity is high, it is necessary to cool $H_xSi(R)_y(OR)_{4-x-y}$ of this invention depending on conditions. - At less than 50 degrees C, advance of gelation is not late practical. On the other hand, if it exceeds 150 degrees C, the independent gel which does not have a crack for rapid solvent evaporation or ebullition will not be obtained. The obtained gel may be further heat-treated and used at an elevated temperature, and said heat treatment temperature has 200 degrees C - desirable 1000 degrees C. At less than 200 degrees C, it is the same as dryness and the effectiveness of heat treatment is not seen. On the other hand, if 1000 degrees C is exceeded, pore will be crushed by sintering etc. and it will not become a porous body.

[0024] Moreover, by drying said raw material on said conditions, after applying to a base mixing, hydrolysis, or the solution that carried out partial hydrolysis; it is also possible to obtain the base which has the porous body film, and this base is just equal to desiccation and heat treatment with plastics, the ceramics, glass, a metal, etc.

[0025] Since a crack cannot generate the porous body and porous body film of this invention easily at the time of desiccation, the independent large-sized thing is obtained. The porous body and porous body film of this invention are the range whose porosity is 40% - 99.9%, and specific surface area is more than $50m^2/g$. Furthermore, the micropore in the range whose aperture is 5nm - 100nm, and an aperture have the high order porosity structure containing the macropore in the range of the diameter of 100 micrometers - 5mm. The property for using suitable for a filter, a demarcation membrane, a sensor, an adsorbent, a catalyst and catalyst support, immobilized enzyme support, an ion exchanger, a heat insulator, an insulator, etc., when porosity is less than 40% and specific surface area is under $50m^2/g$ is not acquired, and on the other hand, when it is 99.9% **, reinforcement required as a porous body and porous body film is not obtained.

[0026] As for the porous body and porous body film of this invention, it is desirable to have the high order porosity structure containing the macropore which has the micropore in the range whose aperture is 5nm - 100nm, and an aperture in the range of the diameter of 100 micrometers - 5mm. a hole [say / that pore is formed because a sol particle with detailed having such high order porosity structure gels, and macropore is formed in the rapid reaction time accompanied by generating of H_2 gas of $H-Si$] -- it is based on a formation mechanism. When the apertures of said micropore are less than 5nm and 100nm **, the property as the porous body which has high order porosity structure, and porous body film is inferior. Moreover, when the aperture of said macropore is less than 100 micrometers, specific surface area becomes under $50m^2/g$, the property as a porous body and porous body film is inferior, and, in 5mm **, the property and reinforcement as a porous body and porous body film are inferior further.

[0027] The silicate water solution used for this invention is a water solution containing one or more sorts chosen from alkaline-earth-metal silicate, such as alkali-metal silicate, such as sodium silicate (water glass) and lithium silicate, barium silicate, and calcium silicate, and the silicate of metal ions other than alkali metal or alkaline earth metal (transition-metals ion and rare earth metal ion, such as aluminum, iron, copper, cobalt, vanadium, titanium, a zirconium, and a cerium). Although especially the concentration of silicate is not limited, its range of 5 - 75 mass % is desirable. If **, one side, and 75 mass % is exceeded that gel with strong reinforcement is hard to be obtained, the stability of a

silicate water solution worsens, or viscosity will be too high and it will be hard coming to produce gel under by 5 mass %.

[0028] In said silicate water solution, $\text{HxSi(R5)}_y(\text{OR6})_{4-x-y}$ is added. Below 80 mass % of the addition is desirable more than 5 mass %, a porous body is not obtained under by 5 mass %, and, on the other hand, the independent porous body which whose reinforcement of a porous body is too weak and does not have a crack when 80 mass % is exceeded is not obtained.

[0029] In said silicate water solution, organoalkoxysilane $\text{Si(R2)}_m(\text{OR3})_{4-m}$ and/or polyorganosiloxane $\text{HO-[Si(R4)}_2\text{O]}_l\text{-H}$ may be added. Although said especially addition is not limited, its 1 - 80 mass % is desirable to a silicate solution. If it volatilizes besides a system, and the addition effectiveness does not show up but 80 mass % is exceeded on the other hand during a reaction, an unreacted amount increases too much and it is not economical at under 1 mass %.

Moreover, the compatibility of organoalkoxysilane $\text{Si(R2)}_m(\text{OR3})_{4-m}$ and/or polyorganosiloxane $\text{HO-[Si(R4)}_2\text{O]}_l\text{-H}$ can be raised by adding organic solvents, such as alcohol, to said silicate water solution. The amount of the organic solvent to be used is a complement, for example, its 0.1-50-mol twice are common to compatibility-izing to the amount of the water of a silicate water solution.

[0030] Next, how to manufacture a porous body from said silicate water solution is described below. First, $\text{HxSi(R5)}_y(\text{OR6})_{4-x-y}$ is added and agitated at -50-50 degrees C in a silicate water solution. A lifting and the foam-ized gel object are acquired for generating and gelation of hydrogen gas by decomposition of Si-H to coincidence.

[0031] It dries at room temperature -150 degree C, and let this foaming gel object be a porous body. The obtained porous body may be further heat-treated and used at an elevated temperature. Said heat treatment temperature has 200 degrees C - desirable 1000 degrees C. At less than 200 degrees C, it is the same as dryness and the effectiveness of heat treatment is not seen, and on the other hand, if it exceeds 1000 degrees C, pore will be crushed by sintering etc. and it will not become a porous body.

[0032] Moreover, by drying said raw material on said conditions, after applying to a base mixing, hydrolysis, or the solution that carried out partial hydrolysis, it is also possible to obtain the base which has the porous body film, and this base is just equal to desiccation and heat treatment with plastics, the ceramics, glass, a metal, etc.

[0033] Since a crack cannot generate the porous body and porous body film of this invention easily at the time of desiccation, the independent large-sized thing is obtained. Said porous body and the porous body film are the range whose porosity is 40% - 99.9%, and specific surface area is more than 50m²/g. Furthermore, it is the high order porosity structure containing the macropore in the range of the pore in the range of the diameter of 5nm - 100nm, and the diameter of 100 micrometers - 5mm.

[0034] The colloidal solution of an oxide particle used for this invention is a particle distributed sol obtained by hydrolyzing the colloidal solutions, such as alumina system sols, such as colloidal silica and boehmite, a titania sol, and a ceria sol, and an alkoxide. Although said especially colloid concentration is not limited, its range of 5 - 75 mass % is desirable. Gel with strong reinforcement is hard to be obtained, and on the other hand, if 75 mass % is exceeded, viscosity will be too high and it will be hard coming for the stability of the colloidal solution to worsen or to produce gel under by 5 mass %.

[0035] To said colloidal solution, $\text{HxSi(R5)}_y(\text{OR6})_{4-x-y}$ is added. The independent porous body which below 80 mass % of the addition is desirable more than 5 mass %, whose reinforcement of a porous body is too weak when a porous body is not obtained under by 5 mass % but 80 mass % is exceeded on the other hand, and does not have a crack is not obtained.

[0036] Next, how to manufacture a porous body from said colloidal solution is described below. First, $\text{HxSi(R5)}_y(\text{OR6})_{4-x-y}$ is added and agitated at -50-50 degrees C to the colloidal solution. A lifting and the foam-ized gel object are acquired for generating and gelation of hydrogen gas by decomposition of Si-H to coincidence. It dries at room temperature -150 degree C, and let this foaming gel object be a porous body. The obtained porous body may be further heat-treated and used at an elevated temperature. Said heat treatment temperature has 200 degrees C - desirable 1000 degrees C. At less than 200 degrees C, it is the same as dryness and the effectiveness of heat treatment is not seen, and on the other hand, if it exceeds 1000 degrees C, pore will be crushed by sintering etc. and it will not become a porous body.

[0037] Since a crack cannot generate the porous body and porous body film of this invention easily at the time of desiccation, a large-sized thing is obtained. Said porous body is the range whose porosity is 40% - 99.9%, and specific surface area is more than 50m²/g. Furthermore, it is the high order porosity structure containing the macropore in the range of the pore in the range of the diameter of 5nm - 100nm, and the diameter of 100 micrometers - 5mm.

[0038] Bulk density ρ_a is calculated from the size and mass of a porous body, and measurement of the porous body of this invention and the porosity of the porous body film can be calculated by $\text{porosity} = 100 \times (1 - \rho_a / \rho)$ from the true density ρ obtained from the pycnometer using gaseous helium. Specific surface area can be measured for example, with a nitrogen gas absorption method. a hole -- size can be measured with a nitrogen gas absorption method, a method of mercury penetration, etc.

[0039] Since a crack cannot generate the porous body and porous body film of this invention easily at the time of desiccation, a large-sized thing is obtained. The porous body containing an organic radical can be used as a waterproof high adsorption ingredient and a waterproof filter ingredient. Moreover, it can be used as the adsorption ingredient or sensor material of a gas or ion. Especially the porous body or porous body film of translucency that has pore 100nm or less can be used as transparency heat insulation aperture material.

[0040]

[Example] Hereafter, although the concrete example of this invention is explained, this invention is not limited only to these examples.

(Example 1) After dissolving the various alkoxides of the presentation (mole ratio) shown in Table 1 into twice as many ten-mol ethanol as this to all alkoxides, it hydrolyzed under the hydrochloric-acid catalyst and the sol was prepared. Hydrolysis ten mol-double-added to all alkoxides, and performed hydrochloric-acid aqueous acids. The sol was put into the plastic container with a cover, and it put at the room temperature. After gelling, it put into every plastic container degrees C [50 degrees C] oven, and was made to dry for five days.

[0041] The obtained sample is Belsorp. Specific surface area and average pore size were measured with the BET adsorption method by nitrogen adsorption using 36. Bulk density ρ_a was computed by having measured the size and weight of a porous body, and $\text{porosity} = 100 \times (1 - \rho_a / \rho)$ was calculated from the true density ρ obtained from the pycnometer using gaseous helium. The check of whether xerogel without a crack is formed was performed visually.

[0042] No.1-11 of an example also had little contraction of the gel at the time of desiccation, there was no crack, it xerogel-ized and the porous body was obtained. Moreover, what also has high porosity and specific surface area was obtained.

[0043] On the other hand, gel contracted No.12-14 of the example of a comparison greatly at the time of desiccation, many cracks occurred, and the independent porous body without a crack was not obtained. Although No.9 had a comparatively high specific surface area, it was easy to generate a crack only in HSi (OC₂H₅)₃. No. -- since 10 and 11 had too few rates of HSi (OC₂H₅)₃, specific surface area was low, and since pore was hardly formed, average pore size was not able to be measured.

[0044] Furthermore, even if it coated the base of plastics, the ceramics, glass, and a metal with this sol of a presentation of Table 1 and formed membranes, the same result as the above was obtained and the base which has the porous body film has been produced.

[0045]

[Table 1]

表 1

	No.	組成 (モル比)								ゼラチン 形成	比表面積 (m^2/g)	気孔率 (%)	平均 細孔径 (nm)
		H-Si	TEOS	MTEOS	DEDMS	HS-Si	H ₂ N-Si	PR'S	M(OR) _n				
実 施 例	1	5	5	—	—	—	—	—	—	○	250.0	60	50
	2	5	—	5	—	—	—	—	—	○	300.5	70	30
	3	7	1	—	3	—	—	—	—	○	451.3	75	60
	4	5	1	—	5	—	—	—	—	○	55.5	40	20
	5	3	1	—	7	—	—	—	—	○	1005.1	80	100
	6	5	1	—	5	—	—	—	—	○	50.6	40	50
	7	10	10	—	—	1	—	—	—	○	86.1	45	10
	8	10	10	—	—	—	1	—	—	○	254.1	65	80
	9	5	—	—	—	—	—	—	5 Ti(OC ₂ H ₅) ₄	○	156.5	50	60
	10	8	—	—	—	—	—	—	2 Zr(OC ₂ H ₅) ₄	○	250.5	55	70
	11	5	—	—	—	—	—	5	—	○	125.5	70	50
比 較 例	12	10	—	—	—	—	—	—	—	× (クラック発生)	105.1	35	50
	13	0.05	10	—	—	—	—	—	—	× (クラック発生)	20.5	10	測定 不可
	14	0.05	—	10	—	—	—	—	—	× (クラック発生)	2.5	1	測定 不可

H-Si : HSi(OC₂H₅)₃
 TEOS : Si(OC₂H₅)₄
 MTEOS : CH₃Si(OC₂H₅)₃
 DEDMS : (CH₃)₂Si(OC₂H₅)₂
 HS-Si : HSC₃H₆Si(OCH₃)₃
 H₂N-Si : H₂NC₃H₆Si(OC₂H₅)₃
 PR'S : HO-[Si(CH₃)₂-O]₃₀-H

[0046] (Example 2) By the presentation of mass % shown in Table 2, HSi(OC₂H₅)₃ 3 was added in the silicate water solution, and it gelled, making it foam at a room temperature.

[0047] This gel object was put into 100-degree C oven, and was dried for 48 hours.

[0048] Measurement of the check of xerogel formation of the obtained sample, specific surface area, average pore size, and porosity was performed by the same approach as an example 1.

[0049] The independent foam gel in which No.15-22 of an example do not have a crack was obtained. When the macropore by foaming was formed and having been observed with the optical microscope, the aperture was the macropore which is 100 micrometers - 5mm. Moreover, what also has high porosity and specific surface area was obtained.

[0050] No.23 of the example of a comparison did not gel and the porous body was not obtained. The independent porous body which whose reinforcement of a gel object is [No.24 of the example of a comparison] weak, and does not have a crack was not obtained. Moreover, although specific surface area was high, porosity was low and pore also became large. No.25 of the example of a comparison were not porosity-ized, therefore specific surface area and porosity also became small.

[0051]

[Table 2]

表 2

	No.	組成 (質量%)						ゼル形成	比表面積 (m^2/g)	気孔率 (%)	平均 細孔径 (nm)
		H-Si	LSS45	LSS75	水ガラス	MTEOS	PR'S				
実施例	15	50	50	—	—	—	—	○	1250.0	90	80
	16	70	30	—	—	—	—	○	1500.0	85	70
	17	10	—	70	—	—	—	○	551.3	99.9	80
	18	30	—	60	—	10	—	○	730.5	95	50
	19	50	—	—	50	—	—	○	1025.1	60	80
	20	80	—	—	20	—	—	○	627.6	40	100
	21	20	—	—	60	40	—	○	845.0	80	10
	22	30	—	60	—	—	10	○	652.5	70	70
比較例	23	1	99	—	—	—	—	× (ゲル化せず)	—	—	—
	24	90	10	—	—	—	—	× (一体化せず)	320.5	35	120
	25	4	—	—	96	—	—	× (多孔化せず)	1.5	10	測定不可

H-Si : $\text{HSi}(\text{OC}_2\text{H}_5)_3$ LSS45 : リチウムシリケート (日産化学製 $\text{Li}_2\text{O}(\text{SiO}_2)_n$, $n=4.5$)SS75 : リチウムシリケート (日産化学製 $\text{Li}_2\text{O}(\text{SiO}_2)_n$, $n=7.5$)MTEOS : $\text{CH}_3\text{Si}(\text{OC}_2\text{H}_5)_3$ PR'S : $\text{HO}[-\text{Si}(\text{CH}_3)_2-\text{O}]_n-\text{H}$

[0052] (Example 3) By the presentation (mass %) shown in Table 3, $\text{HSi}(\text{OC}_2\text{H}_5)_3$ was added to the colloidal solution of an oxide particle, and it gelled, making it foam at a room temperature. This gel object was put into 150-degree C oven, and was dried for 48 hours.

[0053] Measurement of the check of xerogel formation of the obtained sample, specific surface area, average pore size, and porosity was performed by the same approach as an example 1.

[0054] The independent foam gel in which No.26-30 of an example do not have a crack was obtained. When the macropore by foaming was formed and having been observed with the optical microscope, the aperture was the macropore which is 100 micrometers - 5mm. Moreover, what also has high porosity and specific surface area was obtained.

[0055] No.31 of the example of a comparison were not porosity-ized, therefore specific surface area also became small. The independent porous body which whose reinforcement of a gel object is [No.32 of the example of a comparison] weak, and does not have a crack was not obtained.

Moreover, porosity became low although specific surface area was high. No.33 of the example of a comparison were not porosity-ized, therefore specific surface area also became small.

[0056]

[Table 3]

表 3

	No.	組成 (質量%)						ゼル形成	比表面積 (m^2/g)	気孔率 (%)	平均 細孔径 (nm)
		H-Si	シリカ	70ミ	70ニ	70フ	70セ				
実施例	26	30	70	—	—	—	—	○	950.0	80	70
	27	80	20	—	—	—	—	○	1050.0	95	5
	28	50	—	50	—	—	—	○	451.3	60	80
	29	50	—	—	50	—	—	○	330.5	50	60
	30	5	—	—	—	95	—	○	225.1	40	100
比較例	31	4	96	—	—	—	—	× (多孔化せず)	2.5	5	測定不可
	32	85	15	—	—	—	—	× (一体化せず)	120.5	35	10
	33	4	—	96	—	—	—	× (多孔化せず)	3.5	2	測定不可

H-Si : $\text{HSi}(\text{OC}_2\text{H}_5)_3$

シリカ : コロイダルシリカ

アルミナ : ペーマイトゾル

チタニア : チタニアゾル

セリア : セリアゾル

[0057]

[Effect of the Invention] since the porous body of this invention does not need supercritical drying, but it can dry simple by ordinary pressure, -izing can be carried out [porosity] at low temperature and an activity front face is obtained -- various surface qualification -- it is easy to carry out.

Therefore, it can be broadly used for a filter, a demarcation membrane, a sensor, an adsorbent, a catalyst and catalyst support, immobilized enzyme support, an ion exchanger, a heat insulator, an

insulator, a separation column, etc.

[Translation done.]